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DOCTORAL THESIS

Thesis Title

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Declaration of Authorship

I, Jesse GREENSLADE, declare that this thesis titled, "Thesis Title" and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a research degree at this University.

- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.

- Where I have consulted the published work of others, this is always clearly attributed.

- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.

- I have acknowledged all main sources of help.

- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

Signed:

Date:

"Thanks to my solid academic training, today I can write hundreds of words on virtually any topic without possessing a shred of information, which is how I got a good job in journalism."

Dave Barry

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Chapter 1

Introduction and Literature Review

1.1 The atmosphere

The atmosphere is made up of gases held to the earth's surface by gravity. These gases undergo transport on all scales, from barbecue smoke being blown about the garden, to smoke plumes from forest fires travelling across the world and depositing in the Antarctic snow. They take part in innumerable chemical reactions along the way, largely driven by solar input and interactions with each other. Many gases are lofted into the atmosphere by soil, trees, factories, cars, seas and oceans. They are also deposited back to the surface both directly and in rainfall.

The atmosphere is made up of nitrogen (N_2: $\sim$ 78%), oxygen (O_2: $\sim$ 21%), and argon (Ar: $\sim$ 1%), along with water (H_2O) and *trace gases* (those that make up less than 1% of the atmosphere). Water (H_2O) ranges from 0.001 to 1% depending on evaporation and precipitation. Beyond these major constituents the atmosphere has a vast number of trace gases, including carbon dioxide (CO_2: $\sim$ 0.4%), ozone (O_3: .000001 to 0.001%), and methane (CH_4: $\sim$ 0.4%) (Brasseur and Jacob 2017, Ch. 2). Trace gases in the atmosphere can have a large impact on living conditions. They react in complex ways with other elements (anthropogenic and natural), affecting all surface ecosystems upon which life depends.

TODO: Transition from trace gases to ozone and how thesis focuses on ozone in the troposphere. Impacts on the climate due to trop ozone.

Ozone in the lower atmosphere is a serious hazard that causes health problems (Hsieh and Liao 2013), damages agricultural crops worth billions of dollars (Avnery et al. 2013; Yue et al. 2017), and increases the rate of climate warming (Myhre and Shindell 2013). Around 5 to 20 percent of all air pollution related deaths are due to ozone (Monks et al. 2015), roughly .8 million deaths per year (Lelieveld et al. 2013). In the short term, ozone concentrations of $\sim$50-60 ppbv over eight hours or $\sim$80 ppbv over one hour are agreed to constitute a human health hazard (Ayers and Simpson 2006; Lelieveld et al. 2009). Long term exposure causes problems with crop loss and ecosystem damage (Ashmore, Emberson, and Murray Frank 2003), and concentrations may get worse in the future (Lelieveld et al. 2009; Stevenson et al. 2013). Further tropospheric ozone enhancements are projected to drive reductions in global crop yields equivalent to losses of up to USD_{2000} 35 billion per year by 2030 (Avnery et al. 2013), along with detrimental health outcomes equivalent to $\sim$$USD_{2000}$11.8 billion per year by 2050 (Selin et al. 2009). Recently Yue et al. (2017) showed that the net effect of near-surface ozone on is a $\sim$ 14% decrease in net primary productivity in China. They state that reducing this decrease by $\sim$ 70% before 2030 would require drastic measures.

FIGURE 1.1: Pressure (red) logarithmically decreasing, shown with percentage of atmosphere below at several points. Temperature (green) changes throughout the atmosphere. Figure edited from https://climate.ncsu.edu/edu/Structure.

1.1.1   Structure

Most of the atmosphere ($\sim 85\%$) is within 10 km of the earth's surface. This is due to air pressure, which decreases logarithmically with altitude. Any entity is subjected to the weight of all the air above it, and the density of the atmosphere is driven by this pressure.

The atmosphere extends above the earth's surface to the edges of space. This is split into various layers, defined by the *lapse rate*: the decrease in temperature (T) with increasing altitude (z), or $\frac{-\mathrm{d}T}{\mathrm{d}z}$. Figure 1.1 shows the pressure and temperature profiles against altitude through the atmosphere. The first layer is the troposphere, which extends to roughly 10 km and is characterised by positive lapse rate (or decreasing temperature with altitude). At the top of the troposphere (the tropopause) the temperature stops decreasing, and then the stratosphere is defined by a negative lapse rate. This is due to UV radiation being absorbed by ozone, and leads to a very vertically stable environment.

In addition to these atmospheric layers, the troposphere can be subset into the *boundary layer* and the *free troposphere*. The *boundary layer* is the lowest layer and involves increased atmospheric mixing due to ground heating and friction effects. It generally extends anywhere from 200 - 1000 m, above which the ground effects have fewer direct impacts. The *free troposphere* is the remainder of the troposphere and is more affected by transport, both horizontally and from the stratosphere.

1.1.2 Composition and chemistry

TODO overview here There are a myriad of trace gases in the atmosphere, emitted by plants, animals, earth, and water. These gases react with one another and over time they either deposit back onto the earth or form more stable compounds such as CO_2. Oxidation and photolysis are the two main processes whereby compounds are broken down in the atmosphere.

OH and HO_2 concentrations largely determine the oxidative capacity of the atmosphere. The OH radical drives many processes in the atmosphere, especially during the day when photolysis of ozone maintains relatively high OH concentrations (Atkinson 2000). OH is a key species which reacts with nearly all the organic compounds in the troposphere, with only a few exceptions (Atkinson 2000). Over land, isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$) account for 50% and 30% of the OH reactivity (defined in section TODO) respectively (Fuentes et al. 2000).

Since radicals are involved in all oxidative chemistry in the atmosphere it is important for models to accurately represent them (eg. **Travis2014**). This is difficult as they are coupled with so many other species and measurements of OH are not readily available on a global scale. In the late 90's it was thought that OH radicals were formed exclusively from photolysis of O_3, HONO, HCHO, and other carbonyls ($R_2C{=}O$) (Atkinson 2000). It has been shown since that TODO. Isoprene (C_5H_8) was thought to be a sink of OH until it was shown by Paulot et al. (2009b) that the radicals are recycled. This recycling process is discussed in more detail in section 1.3.3.

Ozone is an important precursor to OH, as excited oxygen atoms (O(^{1}D) are created through its photolysis, which then go on to react with water to form OH, as shown in this reaction sequence (Atkinson 2000; Atkinson and Arey 2003):

$$
\begin{aligned}
O_3 + \text{hv} &\rightarrow O_2 + O(^1D) \quad (\lambda \leq 350\text{nm}) \\
O(^1D) + M &\rightarrow O(^3P) + M \quad (M = N_2, O_2) \\
O(^3P) + O_2 + M &\rightarrow O_3 + M \\
O(^1D) + H_2O &\rightarrow 2OH
\end{aligned}
\tag{1.1}
$$

Where *hv* represents radiation and M is an inert molecule. This shows that some of the O(^{1}D) recycles back to ozone, while some forms OH.

1.1.3 Radiative Forcing

One of the larger uncertainties in atmospheric modelling is how particles in the atmosphere affect radiative forcing. For 12 years it has been understood that aerosols overall cool the atmosphere, with smaller particles having a larger effect as they matching the wavelengths of visible light (Kanakidou et al. 2005). Aerosol products from gas phase emissions (or the children thereof) play an indirect and complex role in cloud properties, with a net cooling effect (Kanakidou et al. (2005), Stocker et al. (*IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, Chapter 7,8)).

Transport and indirect effects complicate matters further, with cloud creation and modification of cloud properties being quite difficult to accurately predict. In the third IPCC report (*Intergovernmental Panel on Climate Change (IPCC): Climate Change: The*

Scientific Basis 2001), the uncertainty involved if OA forcing was a factor of 3 times the estimated effect. This has since been improved however OA and cloud formation still remains a large uncertainty in more recent IPCC reports (Forster et al. 2007). Figure 1.2 shows the radiative forcing (RF) of various atmospheric constituents, it is clear that OA uncertainty dominates. Figure 1.3 shows the same summary updated in chapter 8 of the fifth report, where the SOA uncertainty remains quite large.

In order to improve understanding of processes involved in radiative forcing, Kanakidou et al. (2005) highlight the need for improving VOC emissions and flux measurements. They also advocate utilising satellite data in models as a means of improving the emissions inventories. VOCs can lead to changes in cloud formation, as nucleation can arise from the subsequent SOA. Kanakidou et al. (2005) concluded that it is very likely that organics contribute to particle growth and formation rates.

1.2 Ozone

Ozone (O_3) is an important greenhouse gas and oxidant. It is mostly located in the stratosphere and prevents much of the shorter wavelength (UV) solar radiation from reaching the earth's surface. Ozone in the troposphere is less beneficial, leading to health issues, radiative forcing (Stevenson et al. 2013), and crop death. Understanding and accurately portraying ozone concentrations in the troposphere is important to allow accurate predictions of future climate. This will become even more important as projections of future climate changes suggest altered vertical mixing rates, ultra violet index (UVI) and ozone RF (Hegglin and Shepherd 2009).

1.2.1 Stratospheric ozone

In the stratosphere ozone production is driven by the Chapman mechanism, as high energy radiation (with wavelengths $\lambda < 242$ nm) photolyses the molecular oxygen (O_2) in the atmosphere (Brasseur and Jacob 2017, Chapter 3, section 2). The Chapman mechanism involves several reactions which lead to rough equilibrium of O, O_2, O_3 and pressure, as follows:

$$
\begin{aligned}
O_2 + hv &\rightarrow O + O \qquad \lambda < 242\text{nm} \\
O + O_2 + M &\rightarrow O_3 + M \\
O_3 + hv &\rightarrow O + O_2 \qquad \lambda < 1180\text{nm} \\
O + O_3 &\rightarrow O_2 + O_2
\end{aligned}
\tag{1.2}
$$

The high energy photons ($\lambda < 242$ nm) are present from the top of the atmosphere but are mostly removed before reaching the troposphere as their energy is used to split the O_2 molecules. The lifetime of O against loss by O_2 is less than a second in the troposphere, and produced O_3 quickly returns to O and O_2, as low energy ($\lambda < 1180$ nm) photons and M are abundant. The reduced light penetration towards the surface, in addition to the logarithmic increase in atmospheric pressure (which affects M abundance) drives the vertical profile of ozone into what is called the *ozone layer*. This is a layer of relative ozone abundance within the stratosphere. The Chapman mechanism requires radiation so only takes place during the daytime, during the night this

Radiative forcing of climate between 1750 and 2005

FIGURE 1.2: The overall radiative forcings and uncertainties of several atmospheric constituents This is an image taken from Forster et al. (2007), found at https://www.ipcc.ch/publications_and_data/ar4/wg1/en/faq-2-1.html.

FIGURE 1.3: The overall radiative forcings and uncertainties of several atmospheric constituents This is an image taken from Stocker et al. (*IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*), chapter 8.

FIGURE 1.4: Tropospheric ozone processes, Figure 1 in Young et al. (2017). DOI: https://doi.org/10.1525/elementa.265.f1

process slows to a halt, and the ozone concentrations remain stable unless pollution intrudes (Jacob 1999, Chapter 10).

Since the Montreal Protocol on Substances that Deplete the Ozone Layer was established in August 1987, and ratified in August 1989, several satellites and many measurement stations were set up to monitor ozone in the stratosphere. However, in the southern hemisphere there are relatively few records of ozone (Huang et al. 2017). This affects our ability to accurately determine sources of ozone in the troposphere.

1.2.2 Tropospheric ozone

Figure 1.4, copied from Young et al. (2017), shows summary of the major processes and emissions affecting tropospheric ozone. This thesis involves improving the highly uncertain natural emissions of volatile organic compounds (VOCs) from Australia, and estimating impacts from STEs.

Generally there are two main drivers of tropospheric ozone concentrations; transport from the stratosphere and chemical production due to emissions of precursors. Tropospheric ozone is regulated by NO and NO_2 concentrations, which form an equilibrium (Cape 2008; Young et al. 2017). At small to medium scales, pyrogenic (fire) and

FIGURE 1.5: Figure showing NO, NO_2, and Ozone photoequilibrium
cycle with and without (B, A respectively) influence from VOCs. Figure
copied from Atkinson (2000).

anthropogenic (man-made) emissions can be important. Smoke plumes from biomass
burning can carry ozone precursors, creating higher ozone concentrations downwind
of the plume's source. Emissions of precursors from large cities (primarily traffic and
power production) can impact ozone concentrations. These impacts are not always
straightforwards due to the nonlinear relationship between ozone and its precursors.

NO_X ($\equiv NO_2 + NO$) is another important chemical family in the atmosphere which
interacts with ozone and regulates the atmospheric oxidative capacity. NO_X or VOC
emissions affect the tropospheric ozone equilibrium and can lead to enhanced ozone
formation, shown in figure 1.4. NO_X compounds are short lived, with emissions
(Power generation and combustion transport) being the main driver of concentrations
(Delmas, Serca, and Jambert 1997). NO_X is removed primarily by conversion to nitric
acid (HNO_3) followed by wet or dry deposition (Ayers and Simpson 2006).

NO_X and O_3 relative concentrations during the day are regulated by the following
reactions (Sillman 1999; Atkinson 2000):

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + \text{hv} \rightarrow NO + O(^3P) \tag{1.3}$$
$$O(^3P) + O_2 \rightarrow O_3$$

This process with and without the influence of VOCs (panel A and B respectively) is
summarised in figure 1.5.

1.2.3 Stratosphere to troposphere transport

Historically, ozone transported down from the stratosphere was thought to contribute 10-40 ppb to tropospheric ozone levels, matching tropospheric production (Atkinson 2000; Stohl et al. 2003). The proportion of tropospheric ozone due to transport from the stratosphere was revised down to around 10% over the years as measurement and modelling campaigns improved our understanding of global scale transport, mixing, and chemistry (Guenther et al. 2006; Monks et al. 2015). Intrusions of stratospheric air into the troposphere are often called Stratosphere to Troposphere Transport (STT) events. Although most tropospheric ozone comes from production, STT enhancements of ozone are measurable and can be regionally important (eg. Jacobson and Hansson 2000; Lelieveld et al. 2009; Kuang et al. 2017), and upper tropospheric ozone can be transported long distances (Cooper et al. 2004). An analysis of the Atmospheric Chemistry and Climate Model Inter-comparison Project (ACCMIP) simulations by Young et al. (2013) found STT is responsible for 540 ± 140 Tg yr^{-1}, equivalent to ~11% of the tropospheric ozone column (Monks et al. 2015).

Ozone transported to the troposphere from the stratosphere can occur through diffusion (relatively slowly) or direct mixing (as STT). STT often occur as tongues of stratospheric air descend and get disconnected from the stratosphere, potentially due to low pressure systems and jet streams (Sprenger, Croci Maspoli, and Wernli 2003). Recently global chemical transport models (CTMs) have been used to trace how much ozone is being transported to the troposphere in this manner. There are a few methods of doing this, such as modeling ozone formed in (and transported from) the stratosphere (Ojha et al. 2016). Model based estimates require validation against actual measurements, such as those from ozonesondes or satellites. Hegglin and Shepherd (2009) estimate that climate change will lead to increased STT. They posit that this is due to an acceleration in the Brewer Dobson circulation; which is the global scale model of transport of air in the troposphere and stratosphere. They estimate ~ 30, and ~ 121 Tg yr^{-1} increases by 2095 (relative to 1965) in the southern and northern hemispheres respectively, up by 23% globally.

Liu et al. (2017) examine southern hemispheric ozone and the processes which control its inter-annual variability (IAV). IAV is the standard deviation of ozone anomalies from the monthly mean. They show that ozone transported from the stratosphere plays a major role in the upper troposphere, especially over the southern Indian ocean during austral winter. STT mostly impacts the upper troposphere, although some areas are impacted right down to the surface. Kuang et al. (2017) found a measurable impact of STT ozone enhancement in the south east US using several different instruments. They also show how ozone depends on both the local topography, weather systems, and trace gases emitted and transported into the region. Liu et al. (2017) examined modelled tropospheric ozone sensitivity to various meteorological parameters. They found tropospheric ozone sensitivity to emissions from South America (0–20°S, 72.5–37.5°W), southern Africa (5–10°S, 12-38°E), and South to South east Asia (70-125°E, 10°S–40°N). In the US recent work by Lin et al. (2015) suggests that intrusions during spring are increasing surface ozone levels. They recommend improvements to understanding of the frequency and cause of STT are needed effectively implement air quality standards.

1.2.4 Chemical production

Ozone produced in the troposphere from precursors and radiation drive ozone levels, especially in the lower (near-surface) troposphere. The main processes involved are shown in figure 1.4, with ozone regulated by reactions 1.3. As discussed above STTs source $\sim 11\%$ of the tropospheric column of ozone, with the remainder produced photochemically (Monks et al. 2015). A recent summary by Young et al. (2017) estimates ozone production and loss in the troposphere to be $\sim$4900 Tg yr^{-1}, and $\sim$4500 Tg yr^{-1}respectively. These numbers are at the global scale, and it should be noted that meteorology and topography can play massive roles due to large spatial variability in ozone (eg. Kuang et al. 2017).

Tropospheric ozone concentrations require climate and ozone precursor emissions; including NO, NO_2, CO, and VOCs such as HCHO (Atkinson 2000; Young et al. 2013; Marvin et al. 2017). Ozone predictions are uncertain and changing climate affects transport, deposition, destruction, and plant based precursor emissions. All of these processes are tightly coupled and difficult to accurately model, as they depend on uncertain assumptions such as CO_2 dependency (Young et al. 2013). Even with all the work done over the prior decades there remain large uncertainties about ozone precursors in the troposphere (Mazzuca et al. 2016).

Ozone is formed in the troposphere through oxidation of VOCs (described in Section 1.3) in the presence of NO_X. Net formation or loss of O_3 is determined by interactions between VOCs, NO_X, and HO_X, and is a complicated system of positive and negative feedbacks (Atkinson 2000). Figure 1.6 shows an example of this non-linear relationship between NO_X, VOCs, and ozone production as modelled in Mazzuca et al. (2016). This non-linear relationship is examined in more detail in the following section (1.3). Recently the relationship has been examined on the intradiel timescale showing that ozone production can be more or less sensitive to VOCs at different hours (Mazzuca et al. 2016). This shows how important it is to correctly determine the precursors concentrations in order to estimate ozone levels and production.

Tropospheric ozone is lost via chemical destruction and dry deposition, estimated to be 4700 ± 700 Tg yr^{-1} and 1000 ± 200 Tg yr^{-1}, respectively (Stevenson et al. 2006; Young et al. 2017). The main loss channel is through equation 1.1, where photolysis and collisions (increasing with pressure) create OH from the O_3.

1.3 Volatile Organic Compounds

The least well understood precursors to tropospheric ozone production belong to a class of organic compounds. Organic compounds are members of a large class of chemicals whose molecules contain carbon, with the exception of a few compounds such as carbides, carbonates, and simple oxides of carbon and cyanide. Organic compounds can be categorised based on their vapour pressure, which is the tendency of a liquid or solid to vaporise. Compounds with high vapour pressures at standard temperature are classed as volatile, and have a felicity to evaporate at low temperatures. Plants contain tens of thousands of organic compounds, with fewer than 40 having high enough volatility to be emitted (Guenther et al. 2000). Gas phase emissions with

FIGURE 1.6: Ozone production rate dependent on NO_X and VOC concentrations (Mazzuca et al. 2016).

higher vapour pressures can be oxidised into lower vapour pressure products which will partition between gas and particle phase, often called semi or non-volatile.

Atmospheric organic compounds are legion and differ by orders of magnitude with respect to their fundamental properties, such as volatility, reactivity, and cloud droplet formation propensity, etc. Volatile organic compounds (VOCs) have vapour pressure greater than 10^{-5} atm, and are mostly generated naturally by plants, which emit around 1000 Tg yr^{-1}(Guenther et al. 1995; Glasius and Goldstein 2016). Due to their high volatility these compounds generally exist in the gas phase. Organic compounds with a lower volatility are classed as semi-volatile (SVOCs: vapour pressure between 10^{-5} and 10^{-11} atm) are found in both gas and particle phase depending on temperature and pressure. Organic compounds with even lower vapour pressure are generally found in the particle phase in aerosol particulate matter (Glasius and Goldstein 2016). Understanding the drivers of trends in biogenic VOC emissions (BVOCs) is required in order to estimate future carbon fluxes, changes in the water cycle, ozone production, air quality, and other climate responses (Yue, Unger, and Zheng 2015). In the last 20 years anthropogenic emissions of VOCs have been increasing while biogenic VOC emissions have decreased, due to rapid economic growth and lower annual temperatures (Stavrakou et al. 2014; Kwon et al. 2017).

Methane (CH_4) is one of the more abundant VOCs, however it is often classified separately and compared against non-methane VOCs (NMVOCs). NMVOCs include alkanes, alkenes, and aromatic hydrocarbons, with isoprene (an alkene) being the most abundant (Guenther et al. 1995). Methane is relatively long lived (years) and is well mixed in the atmosphere while other VOC levels are spatially diverse due to their shorter lifetimes. In this thesis I work towards a better understanding of the isoprene emissions coming from Australia.

VOCs are an important driver of atmospheric processes, especially near forests. VOCs are broken down into HCHO, O_3, CO_2 and many other species, mainly through oxidation by OH. VOC emissions result in radical cycling, acid deposition, production of tropospheric ozone, and secondary organic aerosols (SOAs) (Atkinson 2000; Kanakidou et al. 2005). VOC emissions affect surface pollution levels, potentially enhancing particulate matter (PM) and ozone levels. A regional-model study in Europe (Aksoyoglu et al. 2017) has also shown VOCs impact secondary inorganic aerosol concentrations. These have impacts on climate (through radiative forcing) and air quality (from ozone and SOA enhancements), affecting both human health and crop yields (Forster et al. 2007; Avnery et al. 2013; Lelieveld et al. 2015).

Ozone in rural areas is often higher than in populous cities, due to titration of ozone by NO in polluted areas (**Cooper2014**; Monks et al. 2015). In areas with high VOC concentrations, ozone production may be enhanced through the following reaction sequence (Sillman 1999):

$$VOC + OH + O_2 \rightarrow RO_2 + H_2O$$
$$RO_2 + NO + O_2 \rightarrow R'CHO + HO_2 + NO_2 \qquad (1.4)$$
$$HO_2 + NO + O_2 \rightarrow OH + NO_2$$

with R and R' representing organic species. The reactions of VOCs or CO with OH convert NO to NO_2, which leads to ozone formation as NO_2 production in reaction 1 of 1.3 is bypassed.

One aspect associated with VOC emissions is the production of aerosols. Aerosols are suspended particulates and liquid compounds in the atmosphere, often called particulate matter (PM). PM in the atmosphere is a major problem, causing an estimated 2-3 million deaths annually (Hoek et al. 2013; Krewski et al. 2009; Silva et al. 2013; Lelieveld et al. 2015). Fine particulate matter ($PM_{2.5}$) penetrates deep into the lungs and is detrimental to human health. Some PM comes from small organic aerosols (OA) emitted in the particulate phase and referred to as primary OA (POA).

A substantial amount of PM is due to gaseous organic compounds transforming in the troposphere leading to what is known as secondary OA (SOA) (Kroll and Seinfeld 2008). Formation of SOA is generally due to VOC oxidation and subsequent reactions, while removal from the atmosphere is largely due to wet or dry deposition, and cloud scavenging (Kanakidou et al. 2005). It can be difficult to attribute the formation of SOA, in part due to the complex relationship between NO_X, OH, O_3, and the uncertainty surrounding precursor emissions. Most of the tropospheric SOA comes from biogenic precursors, the evidence for this has grown over the last two decades (Guenther et al. 1995; Kanakidou et al. 2005; Guenther et al. 2012). Improved concentration estimates of these precursors requires a better understanding of their emissions, which is one of the foci in this thesis.

VOCs are removed by wet and dry deposition, OH oxidation, reaction with NO_3, ozonolysis (at night time or in polluted areas) or photolysis (Atkinson and Arey 2003; Brown et al. 2009). The process of deposition only accounts for a small fraction of the VOC loss, with the possible exception of the long lived methane compound (Atkinson and Arey 2003).

1.3.1 Emissions

VOC emissions are often classified as either anthropogenic, biogenic, or pyrogenic. There are ten times the mass of NMVOCs from natural sources as there are from anthropogenic sources (Guenther et al. 2006; Kanakidou et al. 2005; Millet et al. 2006). Methane and isoprene each comprise around a third of the global total emissions of VOCs (Guenther et al. 2006). Major emitters are broadleafs (notably eucalypts), and shrubs (Guenther et al. 2006; Arneth et al. 2008; Niinemets et al. 2010; Monks et al. 2015). TODO: why do plants emit? increased canopy light penetration? Emissions are affected by various factors such as temperature, sunlight, soil moisture, etc.

Globally around 710 - 1150 Tg C yr^{-1}of BVOCs are emitted (**Lathiere2016**; Guenther et al. 1995; Lathière et al. 2006; Guenther et al. 2012). 90% of these emissions come from plants and trees, with the most dominant species being isoprene (C_5H_8) ($\sim$ 50%), monoterpenes (C_10H_16), methanol (CH_3OH), ethanol (C_2H_6O), acetaldehyde (CH_3CHO), acetone (($CH_3)_2CO$), ethene (C_2H_4) and propene (C_3H_6) (together making up $\sim$ 30%) (Guenther et al. 2012). The larger of these estimates come from MEGAN, a bottom-up biogenic emissions model which is highly sensitive to several parameters including soil moisture and plant functional type. Another model (OR-CHIDEE, with inputs similar to MEGAN) estimates 752 ± 16 Tg C yr^{-1}, sensitive to terrestrial vegetation variations (Lathière et al. 2006).

Global VOC levels are estimated at 85 %, 13 %, and 3 % from biogenic, anthropogenic, and pyrogenic sources respectively (Kanakidou et al. 2005; Kefauver, Filella, and Peñuelas 2014). Methane makes up a third of atmospheric VOCs and is relatively ubiquitous due to its longer lifetime. The main non-methane BVOC emissions are isoprene (44%) and monoterpenes (11%) (Guenther et al. 2000; Kefauver, Filella, and Peñuelas 2014). Land use changes can drastically affect isoprene sources, for instance in the tropics where large scale deforestation has converted forest into crop lands (Kanakidou et al. 2005). In this thesis I'll be focusing on emissions of isoprene.

1.3.2 Isoprene

Isoprene, or 2-methylbuta-1,3-diene, is a VOC with the chemical formula C_5H_8. It is of major importance to the atmosphere, as it is involved in various processes which alter the oxidative capacity of the atmosphere. Isoprene affects NO_X and HO_X cycling, see for example formulae 1.1, 1.3. In the presence of NO_X, isoprene forms tropospheric ozone and SOAs (Wagner 2002; Millet et al. 2006). It has a short lifetime during the day, roughly an hour due to OH oxidation (Atkinson and Arey 2003)).

Guenther et al. (1995), and subsequent updates (Guenther et al. 2000; Guenther et al. 2006; Guenther et al. 2012), have been used ubiquitously by the atmospheric community as a global estimate of isoprene emissions, at roughly 500-600 Tg yr^{-1}, emitted mostly during the day. Recently an estimate of global isoprene emissions, of around 465 Tg C yr^{-1}, has been made using a completely different model (Messina et al. 2016). The global emission factors used to derive both these estimates are based on modelling emissions from different plant species (phenotypes), and relatively few Australian species are used when forming in these estimates.

Measurements of isoprene are often uncertain or difficult to make accurately. Chamber experiments are used to determine how isoprene behaves once it is emitted into

the atmosphere, however reaction rates may be unsuitable to the natural atmosphere which is often very different (Kanakidou et al. 2005; Nguyen et al. 2014). Improving chamber study methods could improve understanding of ambient atmospheric oxidation mechanisms of biogenic hydrocarbons (such as isoprene), which could reduce some of the high uncertainties involved with VOC chemistry (Nguyen et al. 2014). Uncertainties in emissions however require different techniques and measurements in order to be improved.

Isoprene emissions estimates are still fairly uncertain, as global measurements are difficult and regional emissions can be very different. The global uncertainty of isoprene emission was estimated to be a factor of 2 to 5 (250-750 Tg yr^{-1}) (Kanakidou et al. 2005). Improvements over the years have been incremental, and generally localised to regions of particular interest for air quality such as China and the USA TODO: find recent uncertainty estimate improvements examples. The lack of accuracy in BVOC emissions estimates prevents accurate determinations of the sources and distribution of pollutants including ozone and organic aerosols. Accuracy in VOC measurements is important: it has been shown that even the diurnal pattern of isoprene emissions has an effect on modelling ground level ozone (Hewitt et al. 2011; Fan and Zhang 2004).

1.3.3   Isoprene chemistry

Isoprene forms many products with various lifetimes, here I will present an overview of some important mechanisms and products. Isoprene is emitted and enters the atmosphere in the gas phase, where it reacts quickly with OH and other radicals. One common compound which is produced by these reactions is HCHO, which is easier to measure and often used to estimate how much isoprene is being emitted. Figure 1.7 shows the first stage of oxidation of isoprene by OH.

Isoprene reactions are important to understand due to their impacts on air quality, ozone, and physical properties in the lower troposphere. TODO: List some reactions here. The many children processes and products which begin with isoprene oxidation are often called the isoprene (photochemical) cascade (**Paulot2012**; Crounse et al. 2012; Wolfe et al. 2016).

Photolysis and oxidation of many VOCs initially form alkyl radicals ($R\dot{}$). Alkenes (VOCs with double bonded carbon, such as isoprene) react with ozone leading to organic peroxy radicals (ROO˙). In the case of isoprene, these are often labeled as ISOPOO. These go on to form many products and lead to (amongst other things) aerosol, formaldehyde, and ozone formation, depending on sunlight and NO$_X$ concentrations (Atkinson 2000).

Oxidation

The primary first step for atmospheric isoprene is photooxidation, reacting with OH to form isoprene hydroxyperoxy radicals (ROO˙) (**Patchen2017**; Wolfe et al. 2016; Marvin et al. 2017). There is still uncertainty about which pathways are most important following ROO˙ production: HO$_2$ reactions predominantly produce hydroxyhydroperoxides (ISOPOOH), NO reactions largely produce methyl vinyl ketone (MVK) and methacrolein (MCR), and RO$_2$ reactions are also possible Liu et al. (2016b).

FIGURE 1.7: Isoprene products following oxidation by OH, figure from
Mao et al. (2013)

First isoprene has its double bond replaced by OH, as summarised by the equation from PATCHEN et al. (2007): $R-CH=CH-R' + OH \longrightarrow R-CH(OH)CH-R'$ where R and R' represent hydrocarbons. This OH adduct then reacts with O_2 to produce a hydroxyperoxy radical (ROO˙), which can be any of six different isomers (PATCHEN et al. 2007). These ROO˙ (also called organic-peroxy/alkyl-peroxyl/ISOPOO radicals, or RO_2) react with HO_2 or NO and produce stable products (often called oxidised VOCs or OVOCs) (Nguyen et al. 2014). Most of these reaction pathways produce HCHO (Wolfe et al. 2016).

ROO˙ reaction pathways depend on the NO_X concentrations. Reactions with NO can lead to ozone production in environments rich in isoprene or other NMVOCs (PATCHEN et al. 2007; Atkinson and Arey 2003). These reactions are complex and coupled, for example NO_2 concentrations can be increased by NMOC and NO reactions (Atkinson and Arey 2003).

In the presence of NO_X, ROO˙ may form organic nitrates after reacting with NO. Any organic nitrates which are formed affect levels of both HO_X (H, OH, peroxy radicals) and NO_X, generally acting as a sink (Mao et al. (2013) and references therein), although TODO jenny's 2016 paperReaction with NO_2 forms isoprene nitrates, or hydroxynitrate ($RONO_2$). A portion of isoprene nitrates are recycled back to NO_X, so may serve as a reservoir of nitrogen and allow its transport to the boundary layer of remote regions (PATCHEN et al. 2007; Paulot et al. 2009a). The nitrates can also build up in the winter, when removal processes are not as dominant (Lelieveld et al. 2009).

Oxidation reactions are important and quickly stabilise the ratio of NO to NO_2. There is still large uncertainty around the fate of ROO˙, which limits understanding of the relative importance of some chemical processes such as TODO example

Low NOx scenario

Isoprene oxidation by OH is less well understood when lower concentrations of NO are present in the atmosphere. Initially isoprene was thought to be a sink for atmospheric oxidants (e.g. Guenther et al. 2000). It was thought that in low NO environments, like those far from anthropogenic pollution and fires, oxidation of isoprene would create ISOPOOH and lead to low concentrations of OH and HO_2 Paulot et al. (2009b). In Paulot et al. (2009b), the HO_X levels are shown to be largely unaffected by isoprene concentrations. They show that ISOPOOH is formed in yields $> 70\%$, and MACR and MVK is formed with yields $< 30\%$. The formation of MACR and MVK produces some HO_X, although not enough to close the gap. Paulot et al. (2009b) goes on to suggest (and provide experimental evidence) that dihydroxyperoxides (IEPOX) are formed from oxidation of the ISOPOOH, which form precursors for SOAs as well as closing the HO_X concentration gap. They then use GEOS-Chem, modified to include IEPOX formation, to estimate that one third of isoprene peroxy radicals react with HO_2, and two thirds react with NO. They estimated 95 ± 45 Tg yr^{-1}IEPOX being created in the atmosphere, which (at the time) was not modelled by CTMs. Their work showed another pathway for isoprene based SOA creation, through these IEPOX creation and HO_X recycling mechanisms. Peeters and Muller (2010) suggested that the work of Paulot et al. (2009b) only partially bridges the gap between clean air OH concentration measurements and models. They suggested four new mechanisms

for OH recycling in these pristine conditions. These can be summarised as OH regenerating reactions which occur during photolysis of hydroperoxy-methyl-butenals (HPALDs), and resulting photolabile peroxy-acid-aldehydes (PACALDs). These reactions are highly non-linear and subject to large uncertainty, however when compared against several campaigns they were shown to improve modeled HO_X concentrations. In Crounse et al. (2012), MACR products are examined and hydroxy recycling is observed in low NO conditions, backing up results from Peeters and Muller (2010). Peeters and Muller (2010) showed that HO_2 is produced at near unity yields following isoprene oxidation initiated by OH. TODO: read more Peeters2010

Nguyen et al. (2014) examine various measurement techniques to determine isoprene reactions in non-laboratory conditions. Their work discussed how large uncertainties persist in isoprene oxidation, which carries through to predictions by atmospheric models. Nguyen et al. (2014) show preliminary estimates of low-NO yields of MVK and MCR to be 6±3% and 4±2% respectively, consistent with TODO:**Liu2013** but only when cold-trapping methods are employed. These yields each increase (due to interference by OVOCs) to greater than 40% when directly sampled by GC-FID.

Even with the recent boom in isoprene analysis, uncertainties remain in the isoprene oxidation mechanisms. Examples (taken from Nguyen et al. (2014)) include isoprene nitrate yields, which range from 4-15% (Paulot et al. 2009a), 90% disagreements in MAC and MVK yields TODO:(**Liu2013**), various possible sources for SOA TODO:(**Chan2010**; "Reactive intermediates revealed in secondary organic aerosol formation from isoprene"; Lin et al. 2013), unknown HPALD fates, incomplete O_2 incorporation TODO:(**Peeters2009**; Crounse et al. 2013), and under-characterized RO_2 lifetime impacts TODO:(**Wolfe2012**). TODO: get those citations and read abstracts.

Ozononlysis is one of the primary oxidation pathways for volatile alkenes, involving the splitting of carbon chains by ozone molecules (Nguyen et al. 2016). This process also leads to HCHO, with yields depending on reactions following isoprene ozonolysis.

Oxidation by NO3

At night when OH concentrations have dropped, isoprene can remain in the atmosphere. Typically less than half of this night time isoprene is removed through ozonolysis (Atkinson and Arey 2003), however, in polluted areas where high levels of NO_X exist, isoprene is consumed by nitrate radicals (NO_3), which joins to one of the double bonds and produces organic nitrates in high yield (65% to 85%) (Mao et al. 2013). (todo: read mao2013 para 3 cites) NO_3 are largely formed through ozone reactions, as in equation 1.3. A build up of NO_3 radicals can be seen at night, when photolysis is not removing them (Atkinson 2000; Brown et al. 2009).

In areas with high NO_X levels, greater than 20% of the isoprene emitted late in the day ends up being oxidised by the NO_3 radical overnight (Brown et al. 2009). At night isoprene affects on both NO_X concentrations and ozone levels, and can form harmful organic nitrates and SOAs (Brown et al. 2009; Mao et al. 2013). These nitrates go on to produce further SOAs, largely due to NO_3 reacting with first generation isoprene oxidation products (Rollins et al. 2009). The night-time concentrations of OH and ozone also have a complex effect on NO_X removal in high latitude winters, when photolysis and NO reactions are reduced (Ayers and Simpson 2006).

1.4   Formaldehyde

formaldehyde (HCHO), aka methanal, methyl aldehyde, or methylene oxide, is of the aldehyde family. HCHO is an OVOC which is toxic, allergenic, and a potential carcinogen. In this thesis HCHO is used to estimate isoprene emissions over Australia. One of the major products of isoprene chemistry is HCHO. HCHO is important both for its own atmospheric impacts, and as a proxy for determination of isoprene emissions. Given a modelled yield of HCHO from isoprene, it is possible to work backwards from measured HCHO concentrations to determine the isoprene emissions.

1.4.1   Sources and sinks

Background levels of HCHO in the atmosphere are driven by the oxidation of methane (CH_4) by the hydroxyl radical (OH). Atkinson (2000) summarised the background formation of HCHO with the following reaction:

$$OH + CH_4(+h\nu) + 2NO + 2O_2 \rightarrow OH + HCHO + H_2O + 2O_3$$

which shows that photolysis and oxidation of methane forms HCHO and ozone in a process that regenerates the OH radicals. CH_4 concentrations are relatively well constrained in models, with the ACCMIP comparison showing only $\sim$ 3% inter-quartile range (Young et al. 2013). There is a complex relationship between VOCs, HO_X, and NO_X: with higher levels of NO_X increasing the rate at which VOCs are converted into HCHO(Wolfe et al. 2016).

Within the continental boundary layer (CBL), the major source of HCHO enhancement is VOC emissions (which react with OH radicals in the presence of NO_X) (Wagner 2002; Millet et al. 2006; Kefauver, Filella, and Peñuelas 2014). Enhancements to regional and continental HCHO are largely driven by isoprene emissions (Guenther et al. 1995; Palmer 2003; Shim et al. 2005; Kefauver, Filella, and Peñuelas 2014). This is true except near fires or anthropogenic sources of HCHO and precursors (Guenther et al. 1995; Kefauver, Filella, and Peñuelas 2014; Wolfe et al. 2016). Biomass burning (BB) can be a source of HCHO, and various other pollutants, precursors, and aerosols (Guenther et al. 1995; Andreae 2001). Additionally HCHO is emitted into the atmosphere directly through fossil fuel combustion, natural gas flaring, ethanol refining, and agricultural activity (Wolfe et al. 2016).

Other terpenoids (monoterpenes, sesquiterpenes, etc.) can also produce HCHO, although generally to a lesser extent than isoprene, methane and biomass burning (Guenther et al. 2012). Many of the HCHO yields from terpenoids are estimated through chamber studies which examine molecular mass and charge after mixing the compound of choice into a known volume of air (eg. Nguyen et al. 2014). These conditions generally don't match those of the real world, where ambient air will have a cocktail of these compounds and other reactants. One issue with chamber studies is the difficulty they have trying to accurately reproduce ambient outside air, which limits the scope to which the studies may be applied (Nguyen et al. 2014).

Anthropogenic sources of HCHO are largely negligible, however in very large cities or by using oversampling techniques an anthropogenic signal can be found (Millet et al. 2008; Zhu et al. 2014). If the population centres and industrial districts are

large enough they can emit huge amounts of VOCs into the atmosphere (Fu et al. 2007), leading to increased surface ozone levels (Zhu et al. 2014) In Australia this is not yet a major issue, however anthropogenic sources of pollution can be detected (see section 1.7.2.

In the past, HCHO levels were underestimated by models, often with large discrepancies, due to the poor understanding of methyl peroxy radical (CH_3OO) chemistry (Wagner 2002). Nowadays HCHO concentrations are better understood, however precursor emissions are one of the main unknowns (eg. Emmerson et al. 2016; Marvin et al. 2017). Marvin et al. (2017) found that discrepancies in modelled HCHO concentrations are primarily due to second and later generation isoprene oxidation chemistry.

HCHO has two major sinks, one being reactions with OH (oxidation), the other being photolysis: the process of being broken apart by photons (CRUTZEN, LAWRENCE, and PÖSCHL 1999; Wagner 2002; Levy 1972; Kefauver, Filella, and Peñuelas 2014). These reactions lead to a daytime lifetime of a few hours (Atkinson 2000; Millet et al. 2006). Both these loss processes (photolysis, oxidation) form CO and hydroperoxyl radicals (HO_2), and have global significance to radiative forcing and oxidative capacity (Franco et al. 2015). The other notable sinks are wet and dry deposition, although these are not as significant (Atkinson 2000) (TODO: add more cites here).

1.4.2 Measurement techniques

There are a few ways to measure HCHO, including Fourier Transform Infra-Red (FTIR) Spectrometry and Differential Optical Absorption Spectroscopy (DOAS). FTIR examines the Fourier transform of a measured spectrum in order to determine what trace gases are interfering within the IR range of light. DOAS methods are based on light interference and absorption through air masses.

The DOAS technique takes advantage of the optically thin nature of HCHO in order to linearise the radiance differential through air masses with and without HCHO, using the Beer-Lambert intensity law. This method is used both in the home, and from space, globally for HCHO detection (Guenther et al. 1995; Gonzalez Abad et al. 2015; Davenport et al. 2015). As a trace gas HCHO interferes with light over a few wavelength bands, which allows instruments to detect concentrations between a known light source and a detector. Figure 1.8 shows the interference spectrum of HCHO along with a typical band used to examine interference in the DOAS technique. One difficulty is that this interference is relatively small (HCHO is optically thin) and other compounds absorb light at similar wavelengths (Davenport et al. 2015).

FTIR and DOAS measurements have a range of uncertainties, including systematic and random measurement errors and uncertain apriori shape factors and water profiles (eg: Franco et al. (2015)). Other types of measurement involve directly measuring the air, and determining chemical compounds through their physical properties. A proton transfer reaction mass spectrometer (PTR-MS) can be used to determine gas phase evolution of terpene oxidation products (eg. Lee et al. 2006; Nguyen et al. 2014; Wolfe et al. 2016). This is done through analysis of mass to charge ratios (m/z) of ionised air masses which are then identified as chemical compounds. Nguyen et al. (2014) use and compare several instruments (including one which is PTR-MS based) in the analysis of isoprene and monoterpene products. A Gas Chromatography mass

FIGURE 1.8: HCHO spectrum, with a typical band of wavelengths used
for DOAS path measurements. This is a portion of an image from Dav-
enport et al. (2015).

spectrometer (GC-MS) is also able to identify isoprene, monoterpenes, and their products **Lerner2017**; Nguyen et al. (eg. 2014).

Other measurement techniques include chromatographic and fluorimetric methods, both of which differ widely from each other and the spectroscopic methods (Hak et al. 2005). Hak et al. (2005) examine a single air mass with 8 instruments using the four techniques (MAX-DOAS, FTIR, chromatographic, and flourimetric), and show that reasonable agreements can be achieved. Generally the measurements were somewhat close, the five Hantzsch instruments agreeing to within 11% (after removing two potentially faulty measurements), although different calibration standards were used. Titration for the different calibration solutions could not be resolved, which may account for absolute offsets up to 30%. These differences and non-uniformities between measurements (even among identical instruments) are part of the reason HCHO does not have a consistent network for global measurements like those for GHGs or Ozone (Chevallier et al. 2012).

Satellite measurements

Satellites remotely sense atmospheric trace gases through irradiance measurements of solar light which has reflected off the earth's surface. These irradiances are affected by gases which exist along the reflected path of light between the detector, earth, and sun. The irradiance is then used to estimate how much of a particular gas exists along this path, which gives us an estimate which is called a slant column (SC). The retrieved SC of a particular gas (or species) can be transformed into a vertical column (VC) by scaling the path length in conjunction with accounting for the trace gas' light scattering properties. The scaling coefficient created to transform from SC to VC is called the Air Mass Factor (AMF).

Several satellites provide long term trace gas observations with near complete global coverage, including the ERS-2 launched in April 1995 which houses the GOME ultraviolet and visible (UV-Vis) spectrometer, the AURA launched in July 2004 which houses the OMI UV-Vis spectrometer, the MetOp-A and B launched in October 2006 and September 2012 respectively both housing a GOME-2 UV-Vis spectrometer. These satellites are on Low Earth Orbit (LEO) trajectories and overpass any area up to once

FIGURE 1.9: An example spectrum showing interferences used for species concentration measurements by GOME-2. Image by EUMET-SAT and ESA (EUMETSAT 2015).

per day. Satellites can use DOAS techniques with radiative transfer calculations on solar radiation absorption spectra to measure column HCHO . An example of a spectrum retrieved from the GOME-2 instrument is given in figure 1.9.

In conjunction with atmospheric chemistry and radiative models, satellite measurements can be used to quantify the abundance of several chemical species in the atmosphere. Isoprene is hard to measure directly due to its short lifetime and weak spectral absorption, instead HCHO is often used as a proxy (**Surl2018**; Millet et al. 2006; Fu et al. 2007; Dufour et al. 2008; Marais et al. 2012; Bauwens et al. 2013; Kefauver, Filella, and Peñuelas 2014; Bauwens et al. 2016). This leads to a method of isoprene emissions estimation termed top-down (as opposed to bottom-up estimates). The existence of satellite data covering remote areas provides an opportunity to improve VOC emissions estimates leading to more robust models of global climate and chemistry. Satellite data allows us to verify large scale models of natural emissions, and their subsequent chemistry.

1.5 Atmospheric Chemistry Modelling

Models can fill the gaps (both spatial and temporal) in measurement records, and can help us improve our understanding of the world around us. They are used ideally to steer us away from unsustainable pollution by showing us the future outcomes resulting from our emissions, from small to large scales. They can be used to increase measurement accuracy (for instance in satellite measurements) and determine where

we lack information, while also checking the performance of new instruments. Precisely representing various chemicals and reactions in the atmosphere allows efficient mitigation of pollution, since we can compare scenarios against one another. Models can always be expanded to include new compounds or processes, however validation is always necessary. Currently they require improved isoprene emissions and subsequent chemistry understanding for effective air quality determination (Marvin et al. 2017).

Atmospheric chemical models provide a simulation of chemical densities and transport over time, through the atmosphere. They require many inputs (such as wind velocities) in order to accurately represent scenarios or regions on earth. Models of emissions are often used as drivers for atmospheric chemistry models, which require initial and boundary conditions in order to run. Chemistry in the atmosphere is a complex system of coupled reactions and dynamics, which can be solved using numerical partial differential equation solvers.

Chemical Transport Models (CTMs) simulate production, loss, and transport of chemical species. This is generally calculated using one or both of the Eulerian (box) or Lagrangian (puff) frames of reference. CTMs normally solve the continuity equations simultaneously with chemical production and loss for chemicals under inspection. The continuity equations describe transport of a conserved quantity such as mass, which, solved together with production and loss of a chemical can provide detailed simulations of natural processes.

The general continuity equation links a quantity of a substance (q) to the field in which it flows and can be described by the formula:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot j = \sigma$$

where ρ is density of q in the field, t is time, ∇ is divergence, j is the flux (q per unit area per unit time entering or leaving the field), and σ is the generation or loss of q per unit volume per unit time.

The type of model best suited to modelling the entire earth uses the Eulerian frame of reference, where the atmosphere is broken up into 3-D boxes with densities and transport calculated and stored for sequential steps in time at each location. The mass balance equation must be satisfied in any realistic long term box model and is as follows:

$$\frac{dm}{dt} = \sum sources - \sum sinks$$
$$= F_{in} + E + P - F_{out} - L - D$$

where m is mass of a chemical, E and D are emission and deposition, P and L are production and loss, and F is chemical transport in and out, as shown in figure 1.10. Many chemical species interact with each other through production and loss. Any large chemical model will solve this mass balance equation over highly coupled arrays of partial differential equations, which becomes computation time expensive when looking at many species or resolved over many grid-boxes.
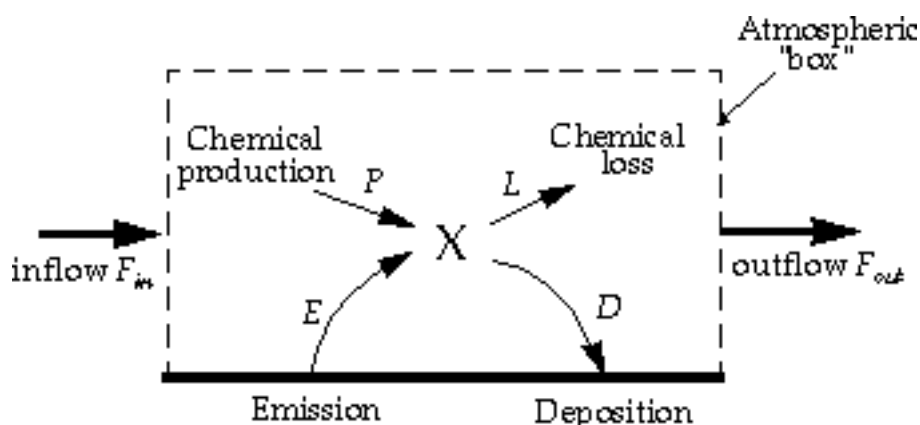
FIGURE 1.10: Standard box model parameters, image taken from Jacob (1999).

Contemporary models generally use mathematical differential solving tools of various complexity to solve chemical equations and reaction rates (often called chemical mechanisms) in order to predict an environments evolution over time. Different solvers may be slower or faster and more suited to particular situations based on the stability of the equations and systems involved, and chemical mechanisms may vary in how many reactions and chemicals are listed and grouped together. For example: Since $[O] << [O_3]$ the chemical family O_X ($O_X \equiv O + O_3$) can be used to simplify chemistry simulations and approximate O_3 concentrations (Brasseur and Jacob 2017, Chapter 3). Zhang et al. (2012) examine the outputs from a regional model (WRF/Chem) using three different chemical mechanisms, and they show some model output sensitivity to the choice of mechanism.

1.5.1 Box models

Box models are much smaller scale than global CTMs, examining one uniform environment with many parametrisations such as transport and emissions. Box models can be used to check chemical mechanisms in specific scenarios, such as high or low NO_X environments. Marvin et al. (2017) use a box model matching conditions in southeast USA to evaluate isoprene mechanisms from several models. A box model involves modelling chemistry in a singular set of conditions without transport or any spatial gradients.

By allowing for interactions between boxes this concept can be extended to multiple-box models. These are simply multiple instances of single boxes with the addition of transport between them, which requires meteorological fields such as wind velocities and turbulence. The meteorology fields can be modelled, and/or input as parameters.

1.5.2 Emissions

There are two commonly used ways of estimating isoprene emissions, top-down or bottom-up. Bottom-up emission estimates generally model the flora and events which emit isoprene, like Eucalypts, factories, shrubs, etc. They use various properties of the emitters in order to estimate how much isoprene is being produced. Some of

these properties include leaf areas, speciated responses to sunlight and temperature, moisture stress, etc (Guenther et al. 1995; Guenther et al. 2006). Understanding how much isoprene is emitted, when and by what, is complicated. One frequently used bottom up emissions model is the Model of Emissions of Gases and Aerosols from Nature (MEGAN, Guenther et al. (1995)). Since little data exists with which to verify many of these bottom-up emission inventories, they can be uncertain on a large scale.

In many CTMs the isoprene emissions are calculated seperately (for example by running MEGAN), and then used as boundary conditions (EG: Guenther et al. (2006)). This can speed up calculations as the transport and concentrations can be simulated in various conditions without recalculating the emissions. Trace gases with short lifetimes and complex chemistry such as isoprene are often hard to measure which makes verifying model estimates difficult.

Bottom up models of VOC emissions are sensitive to parameters. For example Stavrakou et al. (2014) examined modelled Asian emissions and altered model parameters for temperature, plant type emission factors, incoming solar radiation (insolation) intensity, land use changes, and palm tree forest expansion. Changes were constrained by a network of radiation measurements and some experiments with south east Asian forest emissions - and led to reduction in isoprene emissions by a factor of two over the region.

Marais et al. (2014) examine factors affecting isoprene emissions, showing their sensitivity to environmental factors. Their work used MEGAN (Guenther et al. 1995) and GEOS-Chem to look at how these factors affect surface ozone and particulate matter in Africa. One of the important uncertainties seen in MEGAN within this work is the isoprene emissions due to plant type. Canopy level isoprene measurements are made using relaxed eddy accumulation (REA) at several sites in Africa. One plant type near a measurement site emits more than other species and its actual distribution on a larger scale is completely unknown - leading to possible overestimations in MEGAN. Current emissions estimates require more validation against observations, and recently a comparison of two major VOC models (MEGAN and ORCHIDEE) was undertaken by Messina et al. (2016) reiterating this requirement. In their work they examine model sensitivities and show that the important parameters are leaf area index (LAI), emission factors (EF), plant functional type (PFT), and light density fraction (LDF). There is high uncertainty in LAI and EF, which require more or improved measurements at the global scale. LDF paramterisation needs improvement and these models require more PFTs. Global emissions inventories like MEGAN often have large areas based on extrapolations which can introduce uncertainties (Miller et al. 2014).

1.5.3   Uncertainties?

Here I will attempt to list and partially explain the major uncertainties models have in relation to VOCs, SOAs, and ozone. TODO: Is this a good idea or should I put any pertinent uncertainties with the associated work/descriptions?

Emissions Inventories

Using different emissions inventories in an ACM can have large impacts on the simulation. Natural (biogenic or pyrogenic) and human driven (anthropogenic) emissions

often drive a large fraction of atmospheric oxidation and radical chemistry, especially in the continental boundary layer. Zeng et al. (2015) examine the affects on CO and HCHO when running simulations with two different inventories. TODO: find where I took notes about Zeng2015 and put them here.

It is important to note that many estimates of isoprene emission are based on a few algorithms which can depend greatly on input parameters (Arneth et al. 2008; Niinemets et al. 2010). Arneth et al. (2008) argue that this monopoly of emissions estimates may be leading us to an incorrect understanding of isoprene chemistry. Yue, Unger, and Zheng (2015) has shown that this is still a problem by looking at land carbon fluxes and modelling the sensitivity to VOC emissions estimates using two independent models of VOC emission. One model is photosynthesis based and estimates isoprene emissions using electron transfer energies and leaf physiology (Niinemets et al. 1999), while the other (MEGAN) uses the light and canopy temperature ((Guenther et al. 1995; Arneth et al. 2007) TODO: Read Arneth et al., 2007; Unger et al., 2013). Both are sensitive to light and temperature parameterisations.

Resolution

GEOS-Chem simulations are somewhat sensitive to the resolution at which you run. For example: Wild and Prather (2006) show that reduced resolution increases OH concentrations and ozone production rates. Christian, Brune, and Mao (2017) find small changes in OH ($< 10\%$) in OH, HO_2 and ozone concentrations local to the north american arctic, when changing from 4 by 5 to 2 by 2.5 °resolution, however they continue at lower resolution to save computational time.

For many global scale analyses, errors from resolution are less important than those from chemistry, meteorology, and emissions (Christian, Brune, and Mao 2017). Many models lack in-situ measurements with which to verify their chemical mechanisms, leading to large discrepancies, as seen in **Marvin2017a** TODO: briefly talk about Marvin2017a takeaways. Christian, Brune, and Mao (2017) used GEOS-Chem v9-02, with $4° \times 5°$ resolution, and while the low resolution adds errors in OH concentrations and O_3 production rates, the errors from chemistry, meteorology, and emissions are much larger.

Chemistry mechanisms

There is still much work to be done in models to correctly simulate the precursor emissions and processes which lead to HCHO. Often HCHO is used as a way of checking if these precursors are correctly modelled since HCHO measurements are more readily available (for instance from satellites). GEOS-Chem has recently been analysed for ozone and oxidant (OH and HO_2) sensitivity to the processes within the model along with inputs which drive it (Christian, Brune, and Mao 2017). Christian, Brune, and Mao (2017) found that GEOS-Chem ozone was most sensitive to NO_2 photolysis, the $NO_2 + OH$ reaction rate, and various emissions.

Marvin et al. (2017) suggest that isoprene mechanisms in several contemporary models (including GEOS-Chem) are inadequate. They show that for a specific measurement campaign, the HCHO concentrations are underestimated in a way that can

not be easily fixed through rate constant changes. Recently Marvin et al. (2017) compared five global ACMs isoprene mechanisms by evaluating simulated HCHO mixing ratios compared to in situ measurements from the Southeast Nexus (SENEX) aircraft campaign (in southeastern USA). They compared five models (GEOS-Chem, CB05, CB6r2, MCMv3.2, and MCMv3.3.1) and found all of them underestimated the HCHO concentrations (by $15 - 30\%$).

Another important factor in determining the yield of HCHO and other products from BVOCs is the local concentration of NO_X. Travis et al. (2016) show how modelled surface ozone is overestimated due to high estimates of NO_X emissions, which affect oxidative capacity and VOC reactions.

Understanding of OH production/recycling in low NO conditions has been improved (see section 1.3.3), however many observations of OH were still quite underpredicted in models (Mao et al. 2012). Mao et al. (2012) showed how traditional OH measurements may be overestimated due to VOC oxidation. They looked at measurements in a remote forest in California and found that the instruments were generating OH internally. Nguyen et al. (2014) also see this VOC oxidation interference in measurements using a gas chromatographer (GC) with an equipped flame ionisation detector (FID). This lends more credence to the current understanding of VOC oxidation as it closed the gap between measurements and model predictions (Mao et al. 2012).

Clouds

One of the major uncertainties in chemical, climate, radiation, and weather models is cloud formation and dynamics. Clouds are remarkably complex at a much finer scale than can be accurately modelled by global chemistry models (with current processing power). Globally over half (50-60%) of the world is covered by clouds, with $\sim 10\%$ of them being rain-clouds (Kanakidou et al. 2005). Wet scavenging performed in clouds not only depends on large scale cloud processes, but also on the microphysics of aerosols being scavenged, differing between aerosol sizes and hygroscopic properties.

Soil Moisture

Rowntree and Bolton (1983) show how quickly soil moisture anomalies affect rainfall and other weather systems, while Chen and Dudhia (2001) specifically show how important fine scale soil moisture information is when modelling land surface heat flux, and energy balances. Modelled emissions are sensitive to soil moisture, especially near the soil moisture threshold (or wilting point), below which trees stop emitting isoprene and other VOCs completely as they can no longer draw water (Bauwens et al. 2016). MEGAN accounts for soil moisture by applying it as an emission factor which scales the emission rate of various species.

Droughts affects can be difficult to measure, as it is a multi-scale problem which affects various aspects of the land-air interface including plant emissions and dry deposition (Wang et al. 2017). The Standardised Precipitation Evapotranspiration Index (SPEI) is a measure of drought using TODO *SPEI Drought Index*. This product covers 1901 - 2011, and uses the average over that period as the background, in order to

compare drought stressed regions against those with sufficient or excess water *SPEI Drought Index*.

1.6 Australia and the southern hemisphere

Australia has a unique climate, along with soil moisture, clay content and other important properties which affect VOC emissions. These properties are poorly understood in Australia due to the continents size and the relative sparsity of population centres, which make many areas very difficult or expensive to reach. In Australia most long term air quality or composition measurements are performed in or near large cities. Australia is dominated by areas with little anthropogenic influence and no ground based measurements of the natural emissions taking place (VanDerA et al. 2008). Due to the lack of in-situ ground based measurements, estimates of VOC emissions are uncertain, with large scale extrapolation required Millet et al. (2006). Since many Australian cities are on the edge of regions with rich VOC emissions, it is very important to clarify the quantity, type, and cause of VOC emissions. Understanding of emissions from these areas is necessary to inform national policy on air pollution levels.

The trees in Australia are diverse, a great summary is provided by ABARES using the national forest inventory at http://www.agriculture.gov.au/abares/forestsaustralia/australias-forests. Figure 1.11 shows the different forest types and their locations within Australia, highlighting that much of our forested lands are near population centres along the east coast. 16% of Australia is covered by forest, most (75%) of which is Eucalyptus.

Fire emissions include a range of chemicals and each year the affects of fire or burning seasons blanket the northern and southern hemispheres independently. Biomass burning in southern Africa and South America has previously been shown to have a major influence on atmospheric composition in Australia (Oltmans et al. 2001; Gloudemans et al. 2007; Edwards et al. 2006), particularly from July to December (Pak et al. 2003; Liu et al. 2016a). The ocean plays a role in VOC emissions as well, the Asian region is shown to have a strong correlation with the Oceanic Niño Index (ONI), with positive anomalies associated with El Niño (Stavrakou et al. 2014).

Guenther et al. (2006) estimated that the Australian outback is among the worlds strongest isoprene emitters with forests in SE Australia having emission factors greater than $16 \, \text{mg m}^{-2} \, \text{h}^{-1}$ (see figure 1.12). Measurement campaigns in SE Australia have since cast doubt on the emission factors used by MEGAN, as the Eucalyptus trees and soil moisture were poorly studied Emmerson et al. (2016). These emissions factor estimates are not well verified and measurements of isoprene (or other BVOC) emissions barely cover Australia either spatially or temporally. However, comprehensive coverage of one high yield product (HCHO) in the atmosphere over Australia exists in the form of satellite measurements.

1.6.1 Ozone

Ozone levels over Australia are relatively low, however it remains unclear how much we would expect this to change in the future as relatively little is known about precursors and influx for the continent. Australian air quality is monitored independently
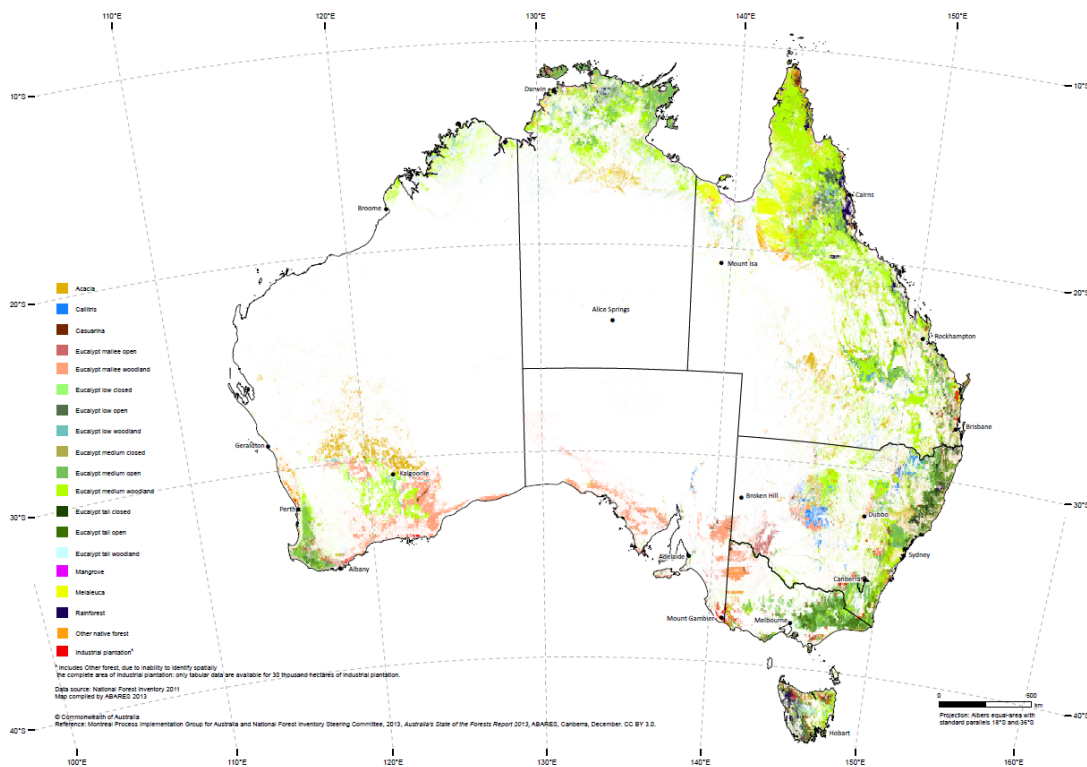
FIGURE 1.11: Forest types in Australia (http://www.agriculture.
gov.au/abares/forestsaustralia/australias-forests)

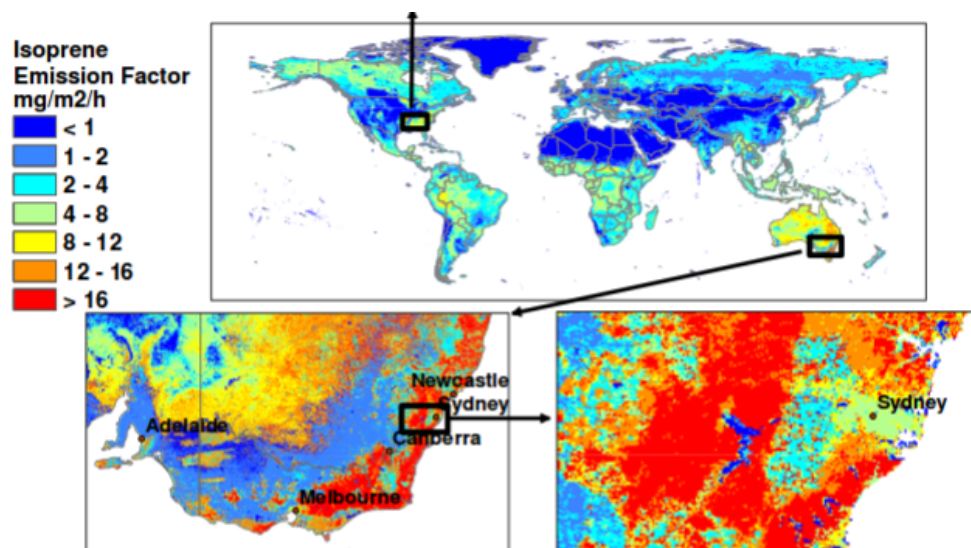**Fig. 2.** Global distribution of landscape-average isoprene emission factors (mg isoprene $m^{-2} h^{-1}$). Spatial variability at the base resolution (∼1 km) is shown by regional images of the southeastern U.S. and southeastern Australia.

FIGURE 1.12: Part of a figure from Guenther et al. (2006) showing global
isoprene emission factors.

within each state, using several metrics. These metrics are measured by varying numbers of monitoring stations in each state. In New South Wales (NSW) the metrics used to determine air quality are: particulate matter (PM), O_3, CO, NO_2, SO_2, and visibility. An air quality index equal to the worst of these metrics is used for NSW as shown at `http://www.environment.nsw.gov.au/aqms/aqitable.htm`. Similar methods are used in other states to get an idea of air quality. Measurement stations are generally located in population centres, and don't regularly measure precursor emissions. This is an important omission as naturally emitted precursor gases often get transported into cities where they affect air quality through production of O_3 and other pollutants.

Generally STT over australia affects the upper troposphere only, however ozone enhancements can reach quite low during heavy storms and cyclonic weather patterns (Alexander et al. 2013).

1.6.2 VOCs

Australia has the potential to be a major hotspot of isoprene emissions according to Guenther et al. (2006) and Guenther et al. (2012), which shows heavy emissions factors in the region. Emissions in MEGAN are based on plant functional types, which can vary heavily even within species. TODO: more on Muller2008 Although recent work suggests that some Australian eucalypts may not be as egregious isoprene emitters as once thought Emmerson et al. (2016). With monoterpenes also being poorly estimated (Winters et al. 2009; Emmerson et al. 2016).

Bottom up inventories of VOCs remain largely uncertain due to extensive extrapolation over plant functional types, changing land cover, and parameterised environmental stressors (Guenther et al. 2000; Kanakidou et al. 2005; Millet et al. 2006). VOC emission estimates are highly sensitive to many factors, several of which are not well characterised in Australia (Sindelarova et al. 2014; Bauwens et al. 2016). Müller et al. (2008) show how isoprene is poorly captured by the MEGAN model and analyse the affect of changing the soil moisture parameter. Sindelarova et al. (2014) show reductions in modelled Australian isoprene emissions of 50% when incorporating soil moisture in MEGAN estimates. Uncertainties in isoprene emissions could explain why models of HCHO over Australia are poor at reproducing satellite measurements (Stavrakou et al. 2009).

Australia suffers from poor characterisation of plant emissions, partly because emission factors are based on northern hemispheric data. Many plant emissions rates have not been published, such as those for any Australian acacias. Some Eucalypt emissions are based on samples from young trees, which may emit more isoprene than older trees (Emmerson et al. 2016). Additionally soil moisture is not well quantified which has a large effect on emissions. Soil type and moisture, along with drought threshholds, have poorly understood effects on plant emissions in Australia Changes in parameterisation of soil moisture in the MEGAN lead to massive changes in Australian isoprene emission estimates (Sindelarova et al. 2014). Over Australia MEGAN suffers from unpublished plant functional types and their emissions (Müller et al. 2008, e.g.). One problem with current estimates of biogenic VOC emissions in Australia is that the emission rates from various species of eucalypt and other flora are highly complex, depending on current and recent weather, temperature, tree age, health, etc. (Guenther et al. 2012). With this complexity added to the diversity of

tree species in Australia as well as sparse rural data collections it is hard to model and verify emissions. Isoprenoid emissions remain to be verified in Australia and monoterpene emissions are 2-4 times too low (Winters et al. 2009; Emmerson et al. 2016). Underestimates of monoterpenes may be due simply to underestimated emission rates for many Eucalypt species (Winters et al. 2009).

Emmerson et al. (2016) analyse EF sensitivity of a high resolution model of atmospheric chemistry over southeast Australia, comparing isoprene and monoterpene emissions against 4 separate campaigns. They show that the effect on total emissions is roughly linear and that no blanket EF changes are appropriate for all regions/seasons. Emmerson et al. (2016) suggest that monoterpenes may be emitted in similar quantites to isoprene, with more measurements required to determine if this is so. They compare emissions estimates from MEGAN against data from several field campaigns and see overestimated isoprene emissions, as well as underestimated monoterpene emissions. Their work suggests that MEGAN estimates of isoprene emissions may be 2-6 times too high, and monoterpene emissions ~ 3 times too low over southeast Australia.

Improvements to emissions models require improved understanding of regions and their behaviour. Inaccuracies can arise due to lack of data, such as the large and sparsely measured Australian outback. Using satellite measurements to fill the gap in Australia can improve understanding of Australian emissions. As HCHO are produced with relatively high yield after isoprene is emitted, satellite measurements of HCHO can allow us to estimate isoprene emissions (Palmer et al. 2001; Millet et al. 2006; Bauwens et al. 2016, e.g.).

1.6.3 Measurements

TODO: Brief overview of all the measurement campaigns, pointing to Modelling and Data chapter for more details. There are relatively few measurements of isoprene in the southern hemisphere, including MUMBA(TODO CITE), SPSS(cite), and that girl from Macquarie University with an instrument in the daintree rainforest(TODO CITE, DESCRIBE). For details on the MUMBA campaign see Section 1.2.2. An airflight campaign (HIPPO) measuring isoprene was also performed in 2009-2011? TODO: ask Jenny re this one.

A particulate and air quality measurement campaign took place in Sydney using PTR-MS and GC-FID, for details see Section 1.2.3.

One method of measuring ozone in the troposphere and stratosphere is by releasing weather balloons (with attached ozone detectors) which take readings as they rise up to around 30 km, giving a vertical profile of concentrations. Since 1986, Lauder, New Zealand (45°S, 170°E) has released ozonesondes allowing a multi-decadal analysis of ozone concentrations over the city (Brinksma et al. 2002). Kerguelan Island (49.2°S, 70.1°E), also has a record of ozonesonde profiles, which are directly in the path of biomass burning smoke plumes transported off shore from Africa (Baray et al. 2012). SHADOZ is the southern hemispheric additional ozone project, which have released sondes from 15 sites at different times `http://tropo.gsfc.nasa.gov/shadoz/`.

A smaller network of ozonesonde release sites is operated by TODO: get details for sondes I use in ozone chapter.

1.7 Aims

TODO: outline of aims here (FIND THESE THEY ARE SOMEWHERE)

One of the aims in this thesis is to use the available satellite measurements to improve the estimates of isoprene emissions in Australia. Satellites which overpass daily record reflected solar (and emitted terrestrial) radiation, and give us measurements over all of Australia. Combining satellite data with model outcomes provides a platform for the understanding of natural processes which is especially useful over Australia. Due to the low availability of in-situ data over most of the Australian continent, a combination of the models with satellite can fill the gap of understanding of emissions from Australian landscapes. Improved emissions estimates will in turn improve the accuracy of CTMs, providing better predictions of atmospheric composition and its response to ongoing environmental change.

Calculation of isoprene to HCHO yields over Australia is required to create top-down estimates. This requires among other things an idea of which VOCs are present and their yields of HCHO. The technique of determining isoprene emissions from satellite detected HCHO is called satellite inversion. **Another aim to this end is to run and become familiar with GEOS-Chem in order to determine Australian emissions and yields, and the importance of the relevant parameters.** Soil moisture plays an important role in VOC emissions, as trees under stress may stop emitting various chemicals. This is especially true for Australia due to frequent droughts and wildfires. The argument for improved understanding of land surface properties, specifically soil moisture, is an old one(Mintz 1982; Rowntree and Bolton 1983; Chen and Dudhia 2001).

To improve understanding of ozone over the southern hemisphere including Australia. Meteorology and precursor emissions are the largest drivers of tropospheric ozone concentrations, and an improved understanding of their effects in Australia would be facilitated by an analysis of STT as well as more confidence in the emitted precursors.

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